

FORM PTO-1390 (Modified) (REV 11-98)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				GLN-005US	
				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 09/743133)	
INTERNATIONAL APPLICATION NO. PCT/CH99/00284		INTERNATIONAL FILING DATE June 30, 1999		PRIORITY DATE CLAIMED July 6, 1998	
TITLE OF INVENTION DEVICE FOR DETECTING A CHEMICAL ELEMENT BY PHOTOEXCITATION					
APPLICANT(S) FOR DO/EO/US Mattias BECK, Jerome FAIST, Antoine MULLER					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1). 4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2)) <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). 7. <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210). 8. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. 9. <input checked="" type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 10. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). 11. <input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409). 12. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)). 					
*Items 13 to 20 below concern document(s) or information included:					
<ol style="list-style-type: none"> 13. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 14. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 15. <input checked="" type="checkbox"/> A FIRST preliminary amendment. 16. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 17. <input type="checkbox"/> A substitute specification. 18. <input type="checkbox"/> A change of power of attorney and/or address letter. 19. <input type="checkbox"/> Certificate of Mailing by Express Mail 20. <input checked="" type="checkbox"/> Other items or information: 					
DEPOSITED BY EXPRESS MAIL NO.: ET159018035US on January 3, 2001					

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U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR <div style="font-size: 2em; font-weight: bold; margin-top: 5px;">09/743133</div>		INTERNATIONAL APPLICATION NO. <div style="font-weight: bold; margin-top: 5px;">PCT/CH99/00284</div>		ATTORNEY'S DOCKET NUMBER <div style="font-weight: bold; margin-top: 5px;">GLN-005US</div>	
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21. The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) : <div style="margin-top: 5px;"> <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1,000.00 <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 </div> <div style="text-align: right; margin-top: 5px;"> ENTER APPROPRIATE BASIC FEE AMOUNT = </div>				CALCULATIONS PTO USE ONLY	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				<div style="border: 1px solid black; padding: 2px;">\$860.00</div> <div style="border: 1px solid black; padding: 2px;">\$0.00</div>	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	13 - 20 =	0	x \$18.00	\$0.00	
Independent claims	4 - 3 =	1	x \$80.00	\$80.00	
Multiple Dependent Claims (check if applicable).				\$0.00	
TOTAL OF ABOVE CALCULATIONS				\$940.00	
Reduction of 1/2 for filing by small entity, if applicable. Applicants are entitled to claim small entity status <input checked="" type="checkbox"/>				\$470.00	
SUBTOTAL				\$470.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				\$0.00	
TOTAL NATIONAL FEE				\$470.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).				\$0.00	
TOTAL FEES ENCLOSED				\$470.00	
				Amount to be: refunded	\$
				charged	\$

☐ A check in the amount of _____ to cover the above fees is enclosed.

☒ Please charge my Deposit Account No. **110227** in the amount of **\$470.00** to cover the above fees.
 A duplicate copy of this sheet is enclosed.


☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **110227** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:


Deborah G. VandenHoff
 Registration No. 45176
 Van Tassel & Associates
 P.O. Box 2928
 Bellaire, TX 77402-2928

 Customer Number: 26003



26003

PATENT TRADEMARK OFFICE


 SIGNATURE

Deborah G. VandenHoff
 NAME

45,176
 REGISTRATION NUMBER

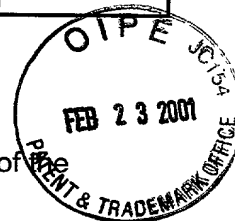
January 3, 2001
 DATE

VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS
(37 CFR 1.9(f) and 1.27 (c))
Small Business Concern

Application No.	09/743,133	Patent No.	
Filing Date	June 30, 1999	Issue Date	
Inventors	BECK, Mattias FAIST, Jérôme MULLER, Antoine	Attorney Docket No.	GLN-00545
Title: DEVICE FOR DETECTING A CHEMICAL ELEMENT BY PHOTOEXCITATION			

I hereby declare that I am:

- ☐ the owner of the small business concern identified below.
☒ an official of the small business concern empowered to act on behalf of the concern identified below.



NAME OF CONCERN: Alpes Lasers
 ADDRESS OF CONCERN: 2, rue de Champréveyres, CH – 2000 Neuchâtel,
 Switzerland

I hereby declare that the above-identified small business concern qualifies as a small business concern as defined in 13 CFR 121.3-18, and reproduced in 37 CFR 1.9(d), for purposes of paying reduced fees under Section 41(a) and (b) of Title 35, United States Code, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the above identified invention described in:

- ☐ the specification to be filed herewith.
☐ the application identified above.
☐ the patent identified above.

If the rights held by the above-identified small business concern are not exclusive, each individual, concern or organization having rights to the invention is listed below and no rights to the invention are held by any person, other than the inventor, who could not qualify as an independent inventor under 37 CFR 1.9(c) or by any other concern which would not qualify as a small business concern under 37 CFR 1.9(d) or a nonprofit organization under 37 CFR 1.9(e).

Each person, concern or organization to which I have assigned, granted, conveyed, or licensed or am under an obligation under contract or law to assign, grant, convey, or license any rights in the invention is listed below:

- ☐ No such person, concern or organization exists.
☐ Each such person, concern or organization is listed below.

*NOTE: Separate verified statements are required from each named person, concern or organization having rights to the invention averring to their status as small entities (37 CFR 1.27).

FULL NAME _____
 ADDRESS _____
☐ Individual ☐ Small Business Concern ☐ Nonprofit Organization

FULL NAME _____
 ADDRESS _____
☐ Individual ☐ Small Business Concern ☐ Nonprofit Organization

FULL NAME _____
 ADDRESS _____
☐ Individual ☐ Small Business Concern ☐ Nonprofit Organization

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING MULLER Antoine
 TITLE OF PERSON SIGNING Directeur Alpes Lasers
 OTHER THAN OWNER

ADDRESS OF PERSON SIGNING: 2, rue de Champréveyres, CH - 2000 Neuchâtel
 Switzerland

SIGNATURE _____

DATE: January the 15th 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No.	PCT/CH99/00284	Group Art Unit	Not yet assigned
Int'l Filing Date	30 June 1999	Examiner Name	Not yet assigned
First Named Inventor	Mattias BECK	Attorney Docket No.	GLN-005US
Title: DEVICE FOR DETECTING A CHEMICAL ELEMENT BY PHOTOEXCITATION			

5

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

10

January 3, 2001

Dear Sir:

The above-identified international application is entering the National Phase under 35 U.S.C. § 371 simultaneously herewith. Kindly amend the application in the following manner:

15

IN THE CLAIMS

8. (Once Amended) Device according to [any of the claims 1 to 7] claim 1, characterised in that it also comprises an enclosure to receive said sample.

20

9. (Once Amended) Device according to [any of the claims 2 to 8] claim 8, characterised in that the enclosure is smaller than the acoustic wavelength at excitation frequency.

25

10. (Once Amended) Device according to [any of the claims 2 to 8] claim 8, characterised in that the enclosure is of such dimension as to accommodate the acoustic modes resonating at excitation frequency.

EXPRESS MAIL

Express Mail No: ET159018035USDate of Deposit: January 3, 2001

This correspondence is being deposited with the Express Mail Post Office to Addressee service of the United States Postal Service under 37 C.F.R. § 1.10 on the date indicated above and is addressed to Assistant Commissioner for Patents, Washington, D.C. 20231


REMARKS

The claims have been amended to change dependencies in claims 8, 9 and 10.

5 It is respectfully submitted that no new subject matter has been introduced by way of this amendment.

Respectfully submitted:

10

By: 
Deborah G. VandenHoff
Attorney for the Applicant
Registration No. 45,176

15 Van Tassel & Associates
P.O. Box 2928
Bellaire, TX 77402-2928
Ph: (713) 839-1749
Fax: (713) 839-1790

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2/12/96

DEVICE FOR DETECTING A CHEMICAL ELEMENT
BY PHOTOEXCITATION

The present invention concerns a device for detecting a chemical element by
5 photoexcitation. More particularly, it relates to a device for measuring the
concentration of elements found in trace form, in a host substance, which may
be solid, liquid or gaseous.

In the present industrial and economic climate, the need to measure the
10 composition or chemical contamination of solids, liquids or gases accurately
has become quite crucial. In fact, it is important to be able to adjust industrial
production processes in real time and also check the quality of the air, water
and ground.

15 Photoexcitation measurement methods are particularly well suited to this type
of detection. Their relative simplicity and selectivity mean that they can be
applied to a very broad range of chemical measuring tasks.

In a photoexcitation detection device, a solid, liquid or gaseous sample of the
20 substance containing the elements investigated, is subjected to the action of
an optical excitation source which emits a light beam, the spectral distribution
of which is selected so as to correspond to the specific absorption band of
molecules observed. The light is partially absorbed by these molecules,
which adopt an excited state. The de-excitation, induced by the molecules
25 observed colliding with those of the host substance, leads to the latter
becoming heated.

It should be specified that the light wavelength should be selected so that the
radiative de-excitation time is much longer than the non-radiative de-excitation
30 time, responsible for heating the medium during the transition from the
rotational to the translational states, induced by collisions.

The heating produces a pressure wave, which is proportional to same. It is
possible, either to detect this pressure wave or any change in the refraction

index of the medium, which is directly due to heating or the pressure change, with the effect detected being proportional to the concentration of the elements being investigated in the host substance.

- 5 A device of this type, used to check air pollution and working with a CO₂ laser, is described in the article by A. Thöny and M.W. Sigrist entitled, "New developments in CO₂ laser photoacoustic monitoring of trace gases", published in Infrared Phys. Technol. Vol. 36, No. 2, pp. 585-615, 1995. Another device used to detect traces of elements in a solid medium is
10 described in document WO 93/22649.

In order to maximise the sensitivity of such a device, it is necessary to maximise the effect created in the sample, so as to optimise the confinement of this effect and its detection. In this respect, the optical source plays an
15 essential part.

In fact, the light produced by the source has a dual action. It excites the molecules investigated in the sample but also generates parasitic effects, mainly the heating of mechanical parts located in the proximity and the
20 heating of molecules of the host substance. Heating the mechanical parts is eliminated by checking the shape of the beam, by using lenses or mirrors, so as to minimise its impact on these parts. It is obvious that this operation would be largely simplified if the source emits in a reduced number of modes. As for heating molecules other than those investigated, this can be avoided by
25 selecting the source emission spectrum, where cover of the absorption spectrum of the element measured is maximum, whilst cover of the absorption spectrum of the host substance is minimum.

What is more, it would be very useful to use a synchronous measuring system
30 or resonant cavity, thereby being able to modulate the source of light. In fact, it is known that the acoustic noise in the case of a pressure measurement, decreases with frequency and that if the resonant cavity is used, its size also decreases with frequency.

In brief, the ideal situation for a photoexcitation source is to be centred around a specific absorption of molecules observed, to emit within a small number of modes and be variable.

- 5 The main limiting factor is the availability of adapted sources of excitation. In fact, the majority of specific absorptions of chemical elements, consisting of several atoms, is found in the mid infrared, a spectrum region also referred to as the chemical fingerprint area. The vibrational and rotational molecule modes are affected by this range of excitation energies and their structure is defined by the composition and shape of the molecule. Unfortunately, this optical spectrum region is very badly covered by conventional sources of sufficient radiance.

- 15 The use of a white light fitted with a filter was suggested, like the one described in document EP 0 685 728. This solution means that the entire infrared spectrum can be continuously reached, but at the cost of very low radiance and the impossibility of quickly modulating the source.

- 20 A gas laser (e.g. CO₂) has the advantage of a high radiance and hence the facility of modulating optical intensity in some cases. However, modulation is limited to fairly low frequencies. What is more, the wavelengths available are quite restricted and do not fully cover the mid infrared.

- 25 Likewise proposed is a tuneable semi-conductor laser, of the type marketed by New Focus Inc. (USA), but since such a source is incapable of reaching the mid infrared, it is necessary to use absorption frequency harmonics and consequently, one has to be content with a very weak efficient section, despite the initial, high radiance.

- 30 The aim of the present invention is to provide a detection device by photoexcitation, which, because of a new type of luminous excitation source, is considerably improved compared with existing versions, both from the point of view of performance and its field of use.

More specifically, the invention relates to a device for detecting by photoexcitation, a chemical element in a host substance, of the type comprising:

- an optical source of excitation comprising a semi-conductor laser, which in the direction of a sample of the substance, emits a light beam whose wavelength, within the mid infrared, corresponds to a specific absorption band of the element; and
- the means of detecting and measuring the heating effects of the host substance, resulting from the interaction of element molecules excited by the beam with said substance molecules.

This device is characterised in that it uses, as a source of optical excitation, a III / V semi-conductor laser.

This could be a semi-conductor quantum cascade laser or a type II quantum well laser, a type II cascade quantum well laser or a multi-quantum laser using materials with low forbidden band energy.

According to a preferred embodiment of the invention, the means of detecting and measuring respond to the pressure wave generated by heating the host substance, which can be in solid, liquid or gaseous form, so as to produce a representation of the concentration of the element in the host substance. These means would preferably include a microphone.

According to another preferred embodiment of the invention, the means of detecting and measuring respond to the variation in the refraction index of the host substance, due to the pressure wave generated by the heating of said substance, so as to produce a representation of the concentration of the element. These means would preferably include a source of light emitting a sounding beam, which crosses the sample and means of measuring the deflection of said beam, which is caused by the variation in the refraction index of the substance.

According to yet a further preferred embodiment of the invention, the means of detection and measuring respond to the variation in the refraction index of the host substance, because of its heating, to produce a representation of the concentration of the element. These means preferably comprise a source of

5 light emitting a sounding beam, which crosses the sample co-linearly to the excitation beam and means of measuring the enlargement of the sounding beam, resulting from the change in refraction index of the substance.

This device may also comprise an enclosure to receive the sample. This enclosure may be smaller than the acoustic wavelength at excitation

10 frequency or be of such dimension that it comprises acoustic modes resonating at the frequency of excitation.

Other characteristics of the invention will become clear from the following description, which has been produced in relation to the enclosed drawings, in which:

15

- Figure 1 shows a schematic diagram of the main constituents of a device for detecting chemical elements by photoexcitation;
- 20 - Figure 2 shows an initial mode of execution of the device according to the invention, in which the heating is detected by the pressure wave it generates;
- Figure 3 shows a second mode of execution, in which the heating is detected by changing the refraction index of the host substance, which causes the pressure wave; and
- 25 - Figure 4 shows a third mode of execution, in which the heating is detected by changing the refraction index it produces.

Reference will first be made to Figure 1, which schematically depicts the composition of a device for detecting chemical elements by photoexcitation. It essentially comprises:

- 5 - a optical excitation source 1 emitting a light beam, the wavelength of which corresponds to a specific absorption band of molecules of the element investigated, which is present in the form of traces;
- a sealed measuring enclosure 2 arranged in the path of the light beam and containing a sample of the solid, liquid or gaseous substance, which acts
- 10 as the host of the element investigated;
- a detector 3 which heats up the host substance and which is arranged on the other side of enclosure 2; and
- an electronic circuit 4 for processing the signal, supplied by detector 3.

15 As already indicated and as will be described in detail below, the device can detect the heating of the host substance, either directly by the pressure wave it generates, or by varying the refraction index of the host substance, which produces the pressure wave, or even by changing the refraction index which brings about the heating.

20 According to the invention, the source of light 1 is a III / V semi-conductor laser, which emits in the mid infrared, in other words, which is capable of working in a wavelength band of between 2 and 12 microns. More specifically, and as a non-limiting example, five different types of mid infrared

25 semi-conductor lasers can be used, namely:

- a quantum cascade laser, hereinafter referred to as QCL, as is described in US patents No. 5 457 709, 5 509 025 and 5 570 386, and in the articles entitled "Laser action by turning the oscillator length", Nature, Vol. 387, 1997, pp. 777-782 and "High power infrared (8 micrometer wavelength)
- 30 superlattice lasers", Science, Vol. 276, 1997, pp. 773-776;
- a QCL fitted with a distributed mirror, as described in the articles entitled: "Distributed feedback quantum cascade lasers", Appl. Phys. Lett. 70, 20, 1997, pp. 2670-2672 and "Complex coupled quantum cascade distributed feedback laser", Photonics Tech. Lett. Vol. 9 N8, 1997, pp. 1090-1092;

- a type II quantum well laser, as described in the article entitled: "Low threshold quasi-CW type II quantum well lasers at wavelength beyond 4 μ ". Appl. Phys. Lett. 71, 22, 1997, pp. 3281-3283;
- a type II cascade quantum well laser, as described in the article entitled
5 "High power mid-infrared interband cascade lasers based on type II quantum wells". Appl. Phys. Lett. 71, 17, 1997, pp. 2409-2411;
- a multi-quantum well laser using materials with low forbidden band energy, as described in the article entitled "High power InAsSb / InPAsSb/ InAs mid-infrared lasers", Appl. Phys. Lett. 71, 17, 1997, pp. 2430-2432.

10 A laser of this type provides all the source advantages indicated above whilst avoiding the drawbacks. It could also be produced in such a way as to emit in the area of chemical fingerprinting, to emit in a small number of modes and be capable of being modulated. What is more, it has the advantage of being
15 small and of consuming little electrical power. This second characteristic is particularly crucial because electrical laser control emits far less parasitic radiation compared with a high-voltage discharge laser.

20 More specifically, the use of a QCL is of particular benefit for the reasons indicated below:

1. The spectral width of the QCL is very small. The multi-mode QCLs fitted with internal Bragg reflectors, in particular, have typical widths of 5 cm^{-1} and 1 cm^{-1} . Consequently, the proportion of optical energy absorbed by
25 the molecules investigated is considerably greater than would be the case with a thermal source, for example.
2. QCLs can be produced at all wavelengths from between 3.5 and 12 microns. This spectrum would light up a vast sample range of absorption rays, fundamental of the organic components found in normal chemistry.
- 30 3. QCLs operate at temperatures close to ambient temperature and consume very little electricity (normally a few watts). It is therefore possible to locate the QCL in a very small enclosure (with a volume of approx. 20 cm^3), which is a considerable advantage compared with the lead salt laser

devices, which require cooling at cryogenic temperatures or optical parametric oscillators [OPO], which require powerful gas lasers.

4. The QCLs are highly independent of their emission wavelength in relation to temperature, which is a very important characteristic, where a system must be capable of operating in a stable manner within a wide temperature range.
5. Compared with a thermal source, the QCL provides far greater excitation of the molecules investigated for comparable volume and energy consumption. The sensitivity of the device has also been considerably improved.
6. Since the efficient excitation section of the molecule investigated is far greater when using a photon, rather than harmonics to excite a fundamental absorption and, given the fact that the available powers of bipolar lasers in the near infrared are also comparable to those of the QCLs, the photo-excitation effect obtained is far greater with a QCL.

Still referring to figure 1, it can be seen that the semi-conductor laser 1 is arranged in an insulated enclosure 5, thereby protecting it from the ambient atmosphere. A transparent window 6 is arranged in one of the sides of the enclosure, along the path of the laser beam, so that the latter can exit through it. The laser 1 is placed on a metal plate 7 made from copper, beryllium or any other highly conductive metal, which in turn rests on a cooling device 8, of the thermo-electric type, for example.

The laser beam emitted penetrates the measuring enclosure 2 through an opening 9, which may be closed by a transparent window. A second opening 10, also possibly closed by a transparent window, is arranged in the wall opposite to that of the inlet opening 9.

Referring now to Figure 2, this shows a first embodiment of the device according to the invention, which can be used in a solid, liquid or gaseous medium. In this case, the pressure wave resulting from heating the host substance is directly detected using a microphone 11 arranged alongside the measuring enclosure 2.

The electrical outlet signal of the microphone 11 is applied to an electronic amplification circuit 12, connected to a display system 13. The pressure wave generated in the enclosure 2 is proportional to the heating of the host substance, which in turn is proportional to the energy absorbed by the molecules of the element investigated. As the latter is present in trace form only, the energy absorbed is proportional to its concentration. Consequently, the intensity of the signal produced by circuit 12 is proportional to the concentration of the element investigated in the host substance. The system 13 now displays the concentration value measured in numeric or analogue form.

In the embodiment just described and according to which the pressure is measured using a microphone, it is possible to work in non-resonant or resonant mode.

In the non-resonant mode, the measuring enclosure 2 is smaller than the acoustic wavelength at working frequency. Therefore, the total contents of the enclosure are generally excited and cooling takes place alongside its walls.

In the resonant mode, however, enclosure 2 is dimensioned such as to accommodate the acoustic modes resonating at working frequency. This configuration allows the acoustic energy to accumulate inside the cavity, thereby improving detection by way of a far more intense signal. Moreover, since it is possible to work at high frequency, the acoustic noise, which decreases with frequency, may be considerably reduced. Since excitation of the molecules only occurs for a small volume proportion, cooling initially takes place by conduction and convection in the host substance and then by conduction against the partitions of the enclosure.

Where measurement has to be conducted in a solid medium, there is no further need to use a measuring enclosure. The excitation beam can now be directly sent to the sample, with the microphone located in the vicinity of same.

Figure 3 depicts a further embodiment of the device according to the invention. In this case, the pressure wave generated by heating the host substance is detected optically.

5

More specifically, use is made of a second source of light 14, which is selected so as to emit a wavelength to which the host substance is transparent. A helium-neon laser could be used. The beam emitted by this source, referred to as the sounding beam, is injected into the enclosure 2
10 through the opening 9, in parallel to the excitation beam emanating from the main source 1. The pressure wave generated by heating compresses the host substance, whose index of refraction is modified in proportion to the concentration of the element investigated. On crossing the enclosure 2, the sounding beam then undergoes a deflection representative of the
15 concentration investigated.

In order to measure this deflection, the sounding beam, when leaving the enclosure 2 through the opening 10, is received by an optical position detector 15, preferably comprising a charge coupled device [CCD] cell line, connected
20 to an analysis circuit 16 connected to a display system 17. The circuit 16 identifies the CCD cell affected by the sounding beam, translates its address into a deflection angle and then into a concentration of the element investigated in the host substance and supplies an output signal representative of this concentration. System 17 then displays the value of the
25 concentration measured in numeric or analogue form.

To conclude, reference is made to figure 4, which represents another form of embodiment of the device according to the invention. In this case, heating of the host substance is likewise detected by a form of optical measurement.

30

More specifically, use is made of a second source of light 18, which is selected so as to emit a wavelength to which the host substance is transparent. A helium-neon laser could be used. The sounding beam thus emitted is injected into the enclosure 2 through the opening 9, so as to be co-

linear with the excitation beam emanating from the main source 1, by way of a dichroic beam separator 19. Heating of the host substance, whether liquid or solid, brings about a proportional change to its refraction index. This variation generates an index gradient divergent lens. The sounding beam, as it passes
 5 through enclosure 2, undergoes enlargement representative of the concentration investigated.

To measure this effect, the sounding beam, as it leaves enclosure 2 through the opening 10, is received by an optical beam-enlarging detector 20,
 10 preferably comprising a line or matrix of CCD cells connected to an analysis circuit 21 connected to a display system 22. The circuit 21 identifies the CCD cells affected by the sounding beam, it then translates their address into an enlargement angle and then into a concentration of the element investigated in the host substance and supplies an output signal representative of this
 15 concentration. System 22 then displays the value of the concentration measured in numeric or analogue form.

As an option, the device of figure 3 could be used according to the principle of the device featured in figure 4. As the sounding beam is no longer co-linear
 20 with the excitation beam, it is now possible to proceed with measuring its deflection caused by the gradient of the index of refraction, which is representative of the concentration of the element investigated.

The modes of execution described with regard to figures 3 and 4, in which the
 25 heating of the host substance is detected optically, can be used in a solid, liquid or gaseous medium, but on condition that it is transparent to the sounding beam.

Naturally, the use of a sealed measuring enclosure – in other words where the
 30 inlet opening 9 and outlet opening 10 are closed by a window, which must be transparent to the sounding beam - would only be justified if working with a liquid or gaseous medium, a corrosive medium or if working under pressure.

CLAIMS

1. Device for detecting by photoexcitation, a chemical element in a host substance, comprising:

- an optical excitation source consisting of a semi-conductor laser, emitting in the direction of a substance sample, a light beam whereof the wavelength, located in the mid infrared, corresponds to an absorption band specific of said element; and
 - the means for detecting and measuring the heating effects of the host substance, resulting from the interaction of the element molecules excited by said beam with said host substance molecules,
- characterised in that the said source of excitation is a quantum cascade laser.

2. Device according to claim 1, characterised in that the said means for detecting and measuring, respond to the pressure wave generated by heating the host substance, to produce a representation of the concentration of said element in said substance.

3. Device according to claim 2, characterised in that the said means comprise a microphone.

4. Device according to claim 1, characterised in that the said means for detecting and measuring respond to the variation in the index of refraction of the host substance, due to the pressure wave generated by the heating thereof, in order to produce a representation of the concentration of said element in said substance.

5. Device according to claim 4, characterised in that the said means comprise a source of light emitting a beam, which crosses said sample and the means of measuring the deflection of said beam, which results from the change in refraction index of the host substance.

6. Device according to claim 1, characterised in that said means for detecting and measuring respond to the variation in the index of refraction of the host substance, resulting from the heating thereof, to produce a representation of the concentration of said element in said substance.

5

7. Device according to claim 6, characterised in that the said means comprise a source of light emitting a sounding beam which crosses said sample in a co-linear manner in relation to the excitation beam and also comprise a means of measuring the enlargement of the sounding beam resulting from the change in the refraction index of the host substance.

10

8. Device according to any of the claims 1 to 7, characterised in that it also comprises an enclosure to receive said sample.

15

9. Device according to any of the claims 2 to 8, characterised in that the enclosure is smaller than the acoustic wavelength at excitation frequency.

10. Device according to any of the claims 2 to 8, characterised in that the enclosure is of such dimension as to accommodate the acoustic modes resonating at excitation frequency.

20

11. Device for detecting by photoexcitation, a chemical element in a host substance comprising:

- a source of optical excitation consisting of a semi-conductor laser which, in the direction of the sample of said substance, emits a beam of light, the wavelength of which, located in the mid infrared, corresponds to an absorption band specific to said element; and
 - the means for detecting and measuring the heating effects of the host substance, resulting from the interaction of the element molecules excited by said beam, with said host substance molecules,
- characterised in that said source of excitation is a type II quantum well laser.

25

30

12. Device for detecting by photoexcitation, a chemical element in a host substance comprising:

- a source of optical excitation consisting of a semi-conductor laser which, in the direction of the sample of said substance, emits a beam of light, the wavelength of which, located in the mid infrared, corresponds to an absorption band specific to said element; and
- the means for detecting and measuring the heating effects of the host substance, resulting from the interaction of the element molecules excited by said beam, with said host substance molecules,

characterised in that said source of excitation is a type II quantum cascade laser.

13. Device for detecting by photoexcitation, a chemical element in a host substance comprising:

- a source of optical excitation consisting of a semi-conductor laser which, in the direction of the sample of said substance, emits a beam of light, the wavelength of which, located in the mid infrared, corresponds to an absorption band specific to said element; and
- the means for detecting and measuring the heating effects of the host substance, resulting from the interaction of the element molecules excited by said beam, with said host substance molecules,

characterised in that said source of excitation is a quantum well laser using materials with low forbidden band energy.

DEVICE FOR DETECTING A CHEMICAL ELEMENT BY PHOTOEXCITATION

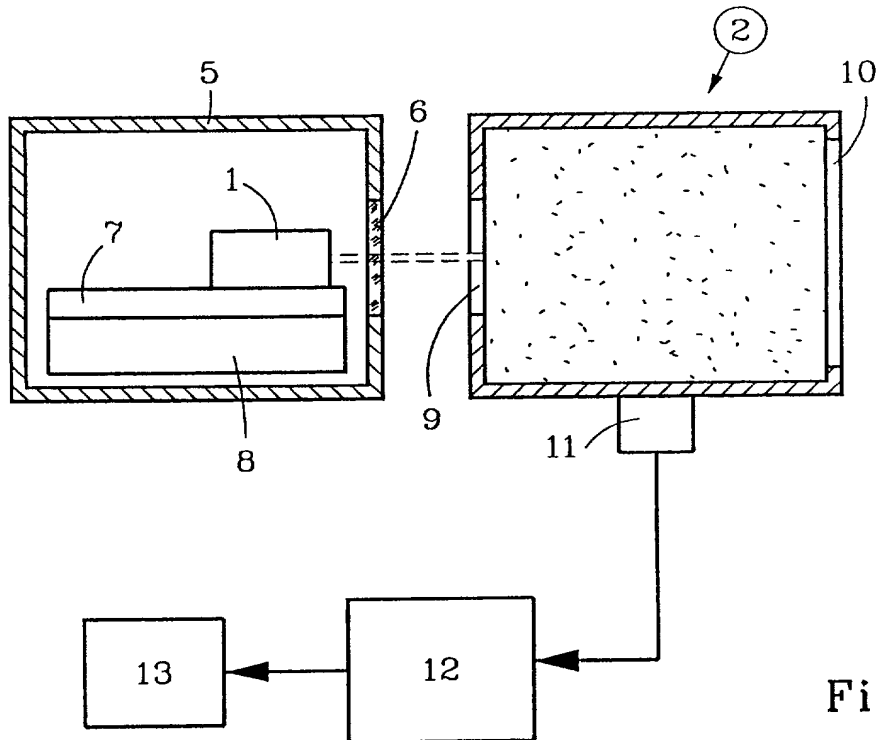
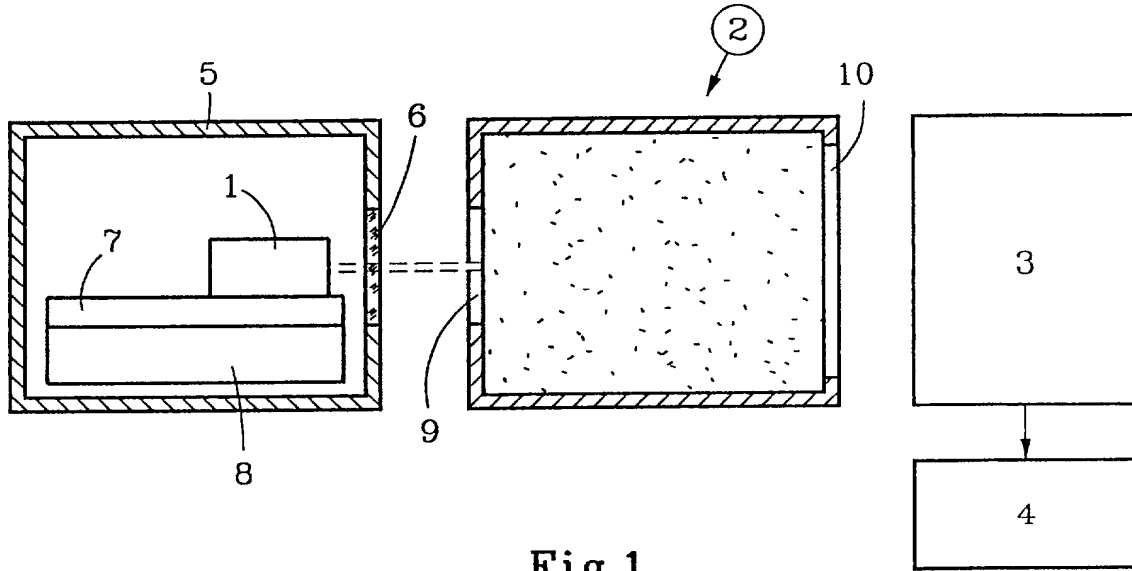
ABSTRACT

5

The invention concerns a device for detecting by photoexcitation a chemical element in a host substrate, comprising : an optical excitation source (1) emitting. In the direction of a substance sample, a light beam whereof the wavelength, located in the mid infrared, corresponds to an absorption band specific of the element; and means for detecting and measuring (11, 12, 13) the heating affects of the host substance, resulting from the interaction of the element molecules excited by said beam said substance. The optical excitation source is a III / V semiconductor laser. It can be a quantum cascade laser, a type II quantum well laser, a type II cascade quantum laser or a multi-quantum laser using materials with low forbidden band energy.

Figure 2

1/2



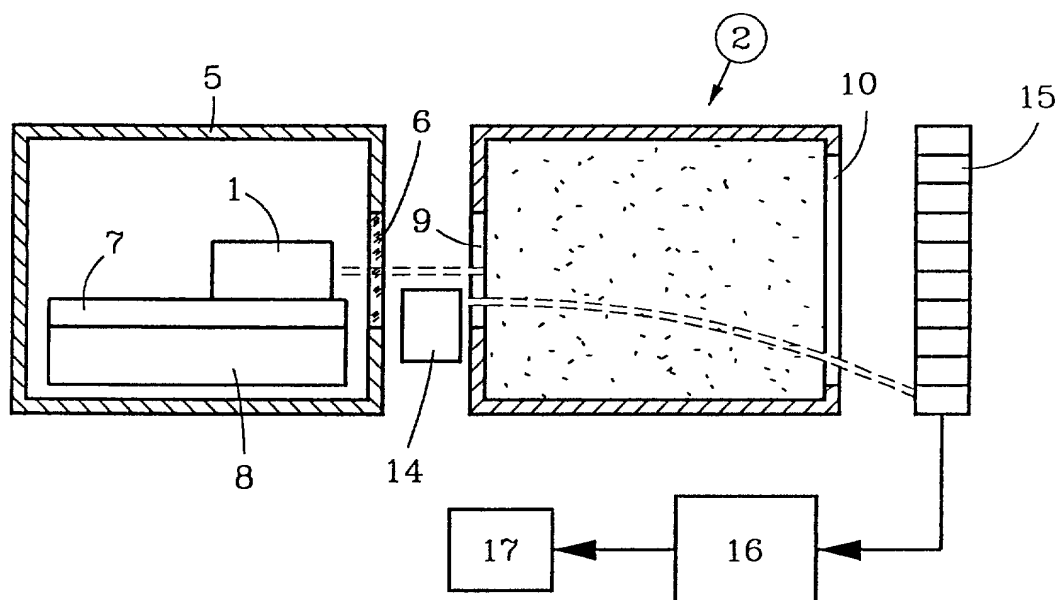


Fig.3

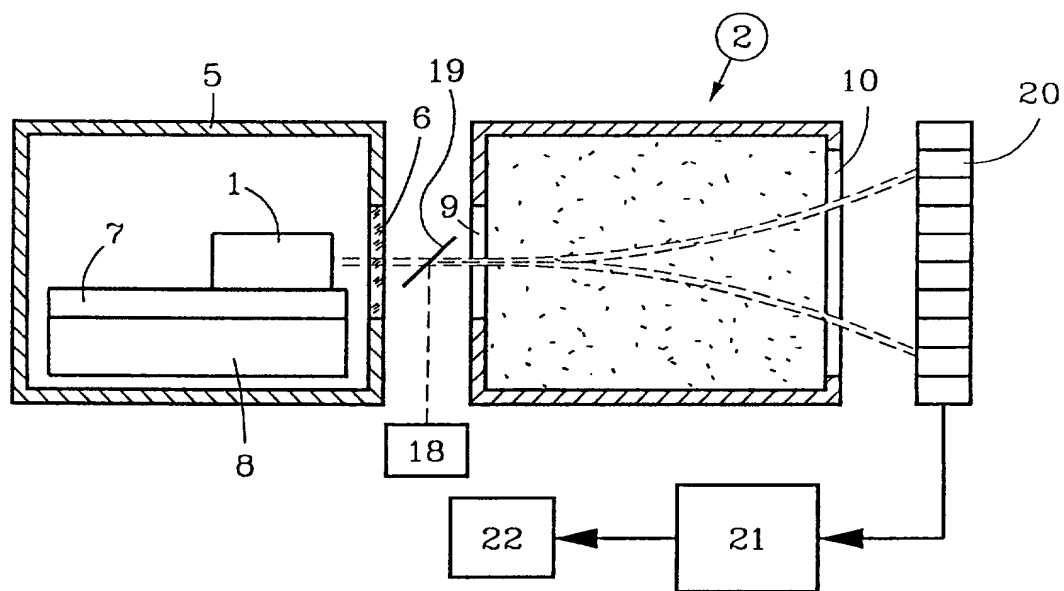
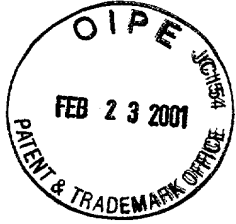


Fig.4

Docket No. GLN-00545
Our case 0147



Declaration and Power of Attorney for Patent Application

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole/joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled

DEVICE FOR DETECTING A CHEMICAL ELEMENT BY PHOTOEXCITATION

the specification of which

☒ is attached hereto.
☒ was filed on 09/14/13 as United States Application No. or
(Filing Date)
PCT International Application No. PCT/CH99/00284 and was amended
(Number)
on _____
(Date, if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in 37 C.F.R. § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

98 08711

France

July 6, 1998

Priority Not Claimed

(Number)

(Country)

(Filing Date)

☐

(Number)

(Country)

(Filing Date)

☐

(Number)

(Country)

(Filing Date)

☐

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below:

(Number) _____ (Filing Date) _____

(Number) _____ (Filing Date) _____

(Number) _____ (Filing Date) _____

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in 37 C.F.R. § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

PCT/CH99/00284 June 30, 1999
(Number) _____ (Filing Date) _____ (Status: patented, pending, abandoned)

(Number) _____ (Filing Date) _____ (Status: patented, pending, abandoned)

(Number) _____ (Filing Date) _____ (Status: patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. § 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY

As a named inventor, I hereby appoint the following attorney(s) and/or agents(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

V **Kurt D. Van Tassel, Registration No. 36,956**
Deborah G. VandenHoff, Registration No. 45,176

Send Correspondence to:

Kurt D. Van Tassel
Van Tassel & Associates
P.O. Box 2928
Bellaire, Texas 77401-2928



Direct Telephone Calls to:

Kurt D. Van Tassel
(713) 839-1776

Alternate: Deborah G. VandenHoff
(713) 839-1749

Full name of sole or first inventor BECK Mattias	
Sole or first inventor's signature <i>[Signature]</i>	Date <i>January 15th, 2001</i>
Residence Realpstrasse 53	
Citizenship Switzerland	
Post Office Address CH - 4054 Basel	

Full name of second inventor, if any FAIST Jérôme	
Second inventor's signature <i>[Signature]</i>	Date <i>January the 15th 2001</i>
Residence 31 Faubourg du Lac	
Citizenship Switzerland	
Post Office Address CH - 2000 Neuchâtel	

Full name of third inventor, if any MULLER Antoine	
Third inventor's signature <i>[Signature]</i>	Date <i>January the 15th 2001</i>
Residence 2, rue de Champréveyres	
Citizenship Switzerland	
Post Office Address CH - 2000 Neuchâtel	